

**RELATION BETWEEN THE ADSORPTION FROM SOLUTIONS
AND THE ADSORPTION OF PURE GASEOUS COMPONENTS
ON THE SAME ADSORBENT. VERIFICATION OF THE DERIVED
RELATIONS IN NONPOLAR SYSTEMS CONTAINING CYCLOHEXANE**

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The isotherms of concentration change from the binary solutions of the cyclohexane with benzene, toluene, chlorobenzene and tetrachloromethane on silica gel have been measured at 20 and 40°C. The results are compared with the values calculated from the measured adsorption isotherms of pure gaseous components on the same adsorbent according to the relations derived previously.

In the previous paper¹, a relation has been derived which makes it possible to compute the isotherm of concentration change in dependence on the composition of the solution from the measured adsorption isotherms of pure components from the vapour phase on the same solid adsorbent. It has been assumed that the adsorption potentials which are necessary for the transfer of one mole of the component from the solution into the surface layer are equal to the adsorption potentials Φ'_1 , Φ'_2 which are necessary to the transfer of one mole of molecules from the pure gaseous phase on the surface of the adsorbent. The derived relation is of the form

$$\Omega = \bar{n}^\omega x_1^\alpha (1 - x_1^\alpha) \int_0^1 \frac{1 - e^f}{x_1^\alpha + (1 - x_1^\alpha) e^f} d\varphi_r, \quad (1)$$

where the quantity Ω is defined as the difference between the amount of the considered substance in the solution before the adsorption and in the equilibrium solution, the difference being referred to the unit mass of the adsorbent, x_1^α is the mole fraction in the equilibrium bulk phase, $\varphi_r = \varphi/\varphi_{\max}$ is the reduced volume, φ_{\max} is the volume of the adsorbed phase, \bar{n}^ω is the average value of the amounts of both pure components adsorbed from the gas phase on the unit mass of adsorbent at the pressure of saturated vapours, and $f = (\Phi'_1 - \Phi'_2)/RT$.

The adsorption potentials of pure substances Φ'_1 , Φ'_2 have been computed as

functions of the adsorption volume from the adsorption isotherms of pure substances according to the relations

$$\Phi'(\varphi) = RT \ln(p/p^0) \quad \text{and} \quad \varphi = a/\varrho, \quad (2)$$

where p is the equilibrium pressure and p^0 is the pressure of saturated vapours at the given temperature, a is the adsorbed amount referred to the unit mass of the adsorbent, and ϱ is the density in the adsorbed phase.

The derived relations have been verified in the previous paper by comparing the computed and the measured Ω -isotherms for six systems. In the present paper, the isotherms of concentration change have been measured in the additional four systems: benzene–cyclohexane–silica gel, toluene–cyclohexane–silica gel, chlorobenzene–cyclohexane–silica gel, and tetrachloromethane–cyclohexane–silica gel at 20 and 40°C, and the results are compared with the values computed according to the relation (1). In addition, the adsorption isotherm of the pure gaseous cyclohexane on the silica gel has been measured at 20 and 70°C. Adsorption isotherms of the pure benzene, toluene, chlorobenzene and tetrachloromethane from the vapour phase are given in the previous paper¹.

EXPERIMENTAL

The silica gel of the particle size 1–2 mm has been washed with the nitric acid, concentrated hydrochloric acid and distilled water, and when dried it has been washed in addition with the mixture of substances used to the adsorption. Before use, it has been dried for 3 hours at 250–300°C. The pure thiophenefree benzene (Lachema), the toluene for UV spectroscopy (Lachema), the pure chlorobenzene (Lachema), and the cyclohexane R. G. (Lachema) have been dried with the molecular sieve 5A and distilled before use in a bubble-cap column with 40 plates (Jena). The tetrachloromethane R. G. (Lachema) has been used without any treatment. The Ω -isotherms have been determined by measuring the change in the composition of the solution before and after adsorption. The solutions prepared by weighing have been sealed together with the dried adsorbent into glass ampoules and thermostated in a constant temperature bath under permanent revolving. When the equilibrium has been reached, the change in the composition of the solution has been determined as the change of the index of refraction by means of the Zeiss interferometer. The adsorption isotherm of the cyclohexane from the gas phase has been measured by weight with the use of the quartz spiral balance. A detailed description of both experimental methods used is given in previous papers^{2,3}.

RESULTS

The results of measurements are given in Tables I and II. From the measured amount of pure cyclohexane, adsorbed from the gas phase on silica gel in dependence on the pressure the adsorption potential Φ' has been computed as a function of the volume of the adsorbed phase according to the equation (2). This dependence has been

expressed by an analytical equation

$$-\Phi' = \Phi^{0'}(\varphi_r^{-1/2} - 1) \quad (3)$$

and the constant $\Phi^{0'}$ has been determined as the slope of the straight line by plotting the Φ' against the $\varphi_r^{-1/2}$.

TABLE I
Adsorption of Pure Gaseous Cyclohexane on Silica Gel^a

20°C, Adsorption								
<i>p</i>	0.032	0.15	0.37	0.72	1.07	2.09	4.20	5.79
<i>a</i>	0.41	1.23	1.63	2.32	2.73	4.23	6.01	7.10
<i>p</i>	8.34	13.32	16.91	23.98	27.79	31.46	36.58	40.11
<i>a</i>	9.56	13.66	17.35	28.41	36.20	45.08	60.79	75.27
<i>p</i>	44.15	48.15	51.84	54.70	58.34	60.42	63.59	65.80
<i>a</i>	95.62	120.75	150.12	178.54	225.94	277.57	358.17	433.70
<i>p</i>	70.08	72.70	75.44	77.59	77.88			
<i>a</i>	472.70	475.00	475.37	477.28	478.10			
20°C, Desorption								
<i>p</i>	77.46	75.57	67.37	60.94	57.06	50.47	45.92	40.78
<i>a</i>	476.73	475.50	473.87	449.82	360.35	204.76	146.53	107.90
<i>p</i>	36.98	28.49	23.37	21.37	20.52	19.73	18.99	18.28
<i>a</i>	85.90	49.86	35.38	31.42	28.55	27.73	25.82	21.99
<i>p</i>	17.68	16.22	11.37	4.82	2.81	1.58	1.15	0.38
<i>a</i>	21.45	19.12	13.94	7.92	4.37	3.42	2.73	1.50
<i>p</i>	0.17	0.10	0.085	0.050	0.032			
<i>a</i>	0.96	1.10	1.10	1.10	1.10			
70°C, Adsorption								
<i>p</i>	1.31	2.21	3.27	4.47	6.33	9.76	12.51	17.96
<i>a</i>	0.27	0.68	0.96	0.96	1.09	2.05	2.32	3.05
<i>p</i>	25.69	32.90	66.06	86.58				
<i>a</i>	3.69	4.78	8.74	11.20				
70°C, Desorption								
<i>p</i>	51.28	36.99						
<i>a</i>	6.56	5.06						

^a *p* is the equilibrium pressure (Torr), *a* is the amount adsorbed (mg/g).

The isotherms of concentration change have been computed according to the equation (1), where the following expression

$$f = \frac{\Phi_1^{0'} - \Phi_2^{0'}}{RT} (\varphi_r^{-1/2} - 1) \quad (4)$$

TABLE II

Isotherms of Concentration Change from Binary Solutions on Silica Gel at 20 and 40°C^a

Benzene(1)–Cyclohexane(2)				Toluene(1)–Cyclohexane(2)			
$x_1^\alpha, 20^\circ$	$\Omega 10^5, 20^\circ$	$x_1^\alpha, 40^\circ$	$\Omega 10^5, 40^\circ$	$x_1^\alpha, 20^\circ$	$\Omega 10^5, 20^\circ$	$x_1^\alpha, 40^\circ$	$\Omega 10^5, 40^\circ$
0.0505	30.29	0.0923	44.76	0.0884	42.48	0.1018	37.22
0.0951	47.88	0.1900	55.26	0.1992	50.30	0.2000	40.22
0.1857	58.65	0.2897	55.24	0.2874	52.56	0.2921	38.78
0.2773	58.28	0.3898	53.63	0.3937	50.56	0.3847	38.08
0.3972	52.43	0.4939	46.98	0.4899	49.98	0.4892	33.59
0.4668	48.37	0.5882	38.16	0.5919	42.28	0.5907	29.07
0.5768	39.80	0.6910	28.45	0.6938	31.28	0.6909	23.23
0.6738	30.29	0.7954	19.04	0.7965	19.22	0.8015	13.86
0.8005	16.21	0.8980	9.98	0.8973	9.96	0.8973	7.22
0.8920	6.98						

Tetrachloromethane(1)–Cyclohexane(2)				Chlorobenzene(1)–Cyclohexane(2)			
$x_1^\alpha, 20^\circ$	$\Omega 10^5, 20^\circ$	$x_1^\alpha, 40^\circ$	$\Omega 10^5, 40^\circ$	$x_1^\alpha, 20^\circ$	$\Omega 10^5, 20^\circ$	$x_1^\alpha, 40^\circ$	$\Omega 10^5, 40^\circ$
0.1080	11.82	0.1071	11.17	0.0895	38.50	0.0920	32.71
0.1955	17.89	0.1962	16.39	0.1857	51.26	0.1887	39.74
0.2960	17.60	0.2955	15.86	0.2912	52.40	0.2907	40.61
0.3980	17.38	0.3991	15.11	0.3779	48.28	0.3802	37.82
0.4938	15.57	0.4932	13.95	0.4925	40.54	0.4940	33.59
0.5974	13.40	0.5978	11.60	0.5929	37.69	0.5935	31.66
0.6894	10.70	0.6905	8.81	0.6951	29.45	0.6946	23.63
0.7986	6.54	0.7984	6.04	0.7959	17.91	0.7969	14.64
0.8966	3.00	0.8967	2.50	0.8980	6.60	0.9016	5.41

^a x^α is the mole fraction of the adsorbed component in equilibrium bulk phase, Ω is the difference of the amount of substance (mol) in the solution before adsorption and in the equilibrium solution referred to the unit mass of adsorbent.

has been substituted for f . The values of $\Phi^{0'}$ for the benzene, toluene, chlorobenzene and tetrachloromethane were determined in the previous paper. The computed curves are compared with the experimental values in Fig. 1.

As it is evident from the figures, the computed and measured Ω -isotherms are of the same sign in all cases, *i.e.* the preferential adsorption takes place with that component, for which the adsorption potential computed from the measurement of the adsorption isotherm from the gas phase has a higher absolute value. In the systems of benzene–cyclohexane–silica gel and tetrachloromethane–cyclohexane–silica gel, the maximum of the Ω -isotherm both computed and found experimentally has practically the same height. In the system toluene–cyclohexane, the height of the computed maximum is approximately by 6 per cent higher, and in the system chlorobenzene–cyclohexane it is by 11 per cent lower. The position of the maximum on the computed Ω -isotherms is shifted in all cases to the middle of the concentration axis. It means that the difference of the computed adsorption potentials is somewhat smaller than in reality.

A rather good agreement of computed and measured curves in most of the ten systems which have been investigated in the present and previous paper proves the suitability of the derived relations for both the qualitative and semiquantitative prediction of adsorption isotherms from binary solutions of nonpolar organic substances on silica gel.

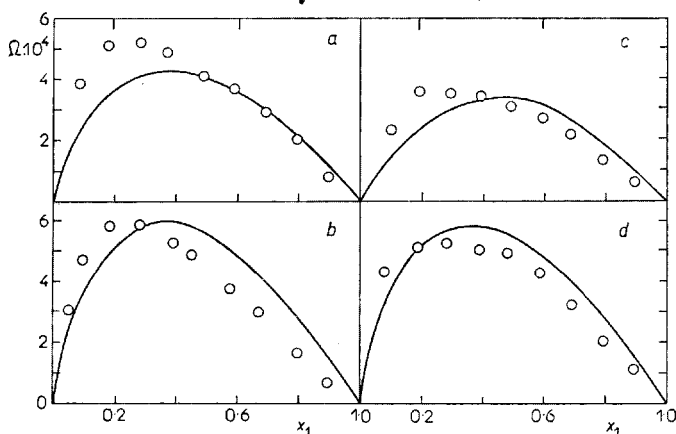


FIG. 1

Comparison of Isotherms of Concentration Change Computed from Measured Isotherms of Pure Components from Vapour Phase with Measured Values for Systems: *a* Chlorobenzene (1)–Cyclohexane (2)–Silica Gel, *b* Benzene (1)–Cyclohexane (2)–Silica Gel, *c* Tetrachloromethane (1)–Cyclohexane (2)–Silica Gel, *d* Toluene (1)–Cyclohexane (2)–Silica Gel

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